

THE EMISSION SPECTRUM OF BISMUTH IODIDE

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Plate XVII

ABSTRACT. The spectrum of bismuth iodide has been photographed in emission in a high frequency discharge using a Fuess spectrograph. A new band system between λ 5900– λ 5600, consisting of four marked groups of bands, some of which are degraded towards the red, is obtained in addition to the band system between λ 4300– λ 4150, analysed by Morgan. Vibrational analysis of this new system has led to the determination of the following constants

$$w, ' = 195.0 \qquad w, '' = 167.9$$

$$\nu, = 17216.0 \quad x, ' w, ' = 1.0 \quad x, '' w, '' \sim 0.3$$

The lower state is considered common to both the systems. By analogy, the new system may correspond to the low frequency system observed in the other bismuth halides. The electronic states in the halides of bismuth are briefly discussed.

INTRODUCTION

In the course of a series of investigations on the molecular spectra of the halides of the elements of groups IV and V of the periodic table, Howell and Rochester (1934) reported that high frequency discharges through the vapours of the halides of lead and bismuth excited in each case large systems of bands degraded towards the red. Later, Howell (1936) published the analysis of a band system between λ 5100– λ 4150, attributed to the diatomic molecule, BiF. The band spectra of BiBr, BiCl, BiF and BiI have been examined by Morgan (1936) in absorption and a vibrational analysis given for each of the observed systems. For BiBr, two systems for each of the isotopes $\text{Br}^{79}\text{Cl}^{35}$ and $\text{Br}^{81}\text{Cl}^{37}$ with origins at λ 4045.7 Å and λ 4869.1 Å, were analysed. In BiCl, a band system lying between λ 4000– λ 3600 has been found for each of the isotopes Cl^{35} and Cl^{37} in addition to the system at λ 5500– λ 4300 reported by Saper (1931). The vibrational analyses in the above two cases have been confirmed by the respective isotope shifts. One band system between λ 4900 and λ 4150 for BiF has been analysed. The analysis of this system is entirely in agreement with that reported by Howell for BiF in emission. Morgan also reports another system for BiF, on the shorter wave-length side of the above system, but no analysis is given as it is too weak for measurement. Rochester (1937) reports a triplet system

for BiF in the ultraviolet between λ 3050– λ 2250 with wide multiplet separations of 7300cm^{-1} and 4800cm^{-1} . In the case of BiI, only one band system between λ 4300– λ 5150 has been observed. It corresponds to the high frequency system observed in the other bismuth halides. The bands, which are about 22 in all, are arranged in marked sequences but the direction of degradation of the bands is uncertain. The following quantum formula has been derived by Morgan to represent the bands:

$$\nu = 23388.9 + (198.6u' - 1.44u'^2) - (163.9u'' - 0.31u''^2)$$

Morgan suggested that the low frequency system, corresponding to the one observed in the other halides of bismuth, might have been either lost in the overlapping diatomic bismuth bands occurring in the same region, or altogether absent because of the probable decomposition of BiI, at the high temperatures used in his experiment. No previous work on the emission spectrum of this molecule appears to have been published so far.

As a continuation of his work on the molecular spectra of such a series of molecules as TlI, PbI the author investigated the emission spectrum of BiI, excited by a low-power H.F. Oscillator. A new band system attributed to the diatomic molecule BiI, which corresponds to the low frequency system observed in the other bismuth halides has been obtained in addition to the system λ 4300– λ 4150 reported by Morgan in absorption. The object of this paper is to report the analysis of the new system.

The experimental method for this investigation also is the same as the one employed by the author in the case of TlI and described in detail elsewhere (Rao and Rao, 1949). Working with the iodides of heavy elements, it has been the experience of the author that the emission bands and continuum of iodine, which is invariably present in the discharge tube as a decomposition product, could be eliminated by a careful heating of the substance and by giving minimum exposure with a sharply focussed spectrograph. With BiI, continued heating was found necessary for maintaining a characteristic discharge which is bluish violet in colour. In photographing the spectrum a Fuess glass spectrograph was mainly used. The advantage of using this instrument was the short interval of time during which optimum conditions for reproducing the spectrum could be maintained. An exposure of 5 minutes duration was found sufficient using Kodak-panchromatic plates. In addition to the bands, some bismuth lines were also excited. Measurements were made on a Hilger comparator and were reduced to wavelengths by using iron arc standards. Band head data obtained from different plates seldom differed by more than 2 wave-number units.

DESCRIPTION OF THE SPECTRUM

The spectrum is reproduced in two strips in Figs. *a* and *b* (Plate XVII). Strip *a* is an enlargement of the system between λ 5900– λ 5650 newly obtained

in the present investigation. The bands are arranged in four distinct groups. Some of the bands appear clearly red-degraded while the direction of degradation of some others is uncertain. Strip *b* is a reproduction of the system between $\lambda 4300 - \lambda 4150$ analysed by Morgan. The bands are clearly red-degraded, while the sequence degradation is towards the violet. But Morgan reports that the direction of degradation of these bands obtained by him in absorption is uncertain. This system is reproduced here to show that the bands appear more prominently in emission than in absorption.

Table I gives the wavelength, intensity and other data of the new system.

TABLE I
(Bismuth iodide bands)

Wavelength	Int.	Wavenumber	Classification	Obs. - Calc
5859.9	6	17060.4	0,1	-1.6
50.3	5	17088.4	1,2	0.1
41.2	4	17115.0	2,3	1.8
33.2	2	17138.5	3,4	1.8
5802.2	10	17230.1	0,0	0.8
5794.4	4	17256.6	1,1	1.6
37.8	8	17423.5	1,0	1.2
30.2	4	17446.6	2,1	0.6
23.6	1	17466.7	3,2	-1.6
5676.6	4	17611.3	2,0	-2.0
68.9	3	17635.2	3,1	0.2

Vibrational Analysis and Intensity Distribution

The bands are arranged in four marked groups. The relative intensities of bands in each group suggest that each group is obviously to be regarded as a sequence. Intensity considerations point to the group of bands at $\lambda 5800$ as being the $\Delta v = 0$ sequence. The group lying on its longer wavelength side is then to be identified as the (0,1) sequence. From intensity considerations the most intense band in this sequence is to be classified as the (0,1) band. The intensities of the higher sequence members gradually fall off. A similar feature is observed in all the other sequences. Some of the higher sequence members present a line like appearance as their direction of degradation

tion is uncertain. The (0,0) band appears clearly red degraded while the direction in which the (1,0) band is degraded is uncertain. It is to be noted that in all cases, the sequence degradation is towards the violet, though some of the bands are clearly degraded towards the red. The vibrational matrix shown in Table II is built up to include all the band heads. As the number of bands observed in the system is small, only two $\Delta G(v'')$ values are obtained and of these two the first is probably more reliable. Since the direction of degradation of some of the bands is uncertain, the breadth of such bands being of the order of 5 wavenumber units, the lower state vibrational frequency suggested here may be regarded as approximately equal to that of the other system analysed by Morgan. Hence the lower state appears to be common to both the systems. The upper state vibrational frequency obtained here is also of the same order as that of the other system. By analogy, this system may correspond to the low frequency system observed in the other bismuth halides. The following vibrational constants are suggested for the system

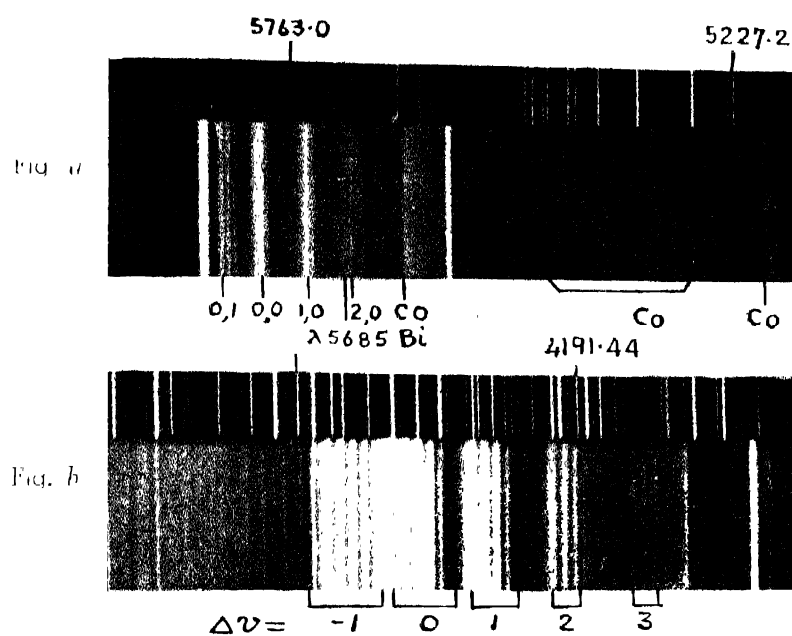
$$\begin{aligned}\omega'_e &= 195.0 & \omega''_e &= 167.9 \\ \nu_e &= 17216.0 \\ x'_e \omega'_e &= 1.0 & x''_e \omega''_e &= 0.3\end{aligned}$$

It is to be noted that while in the corresponding systems of the bismuth halides $\omega'_e < \omega''_e$, in this system $\omega'_e > \omega''_e$.

The intensity distribution in the system is shown in Table III. The intensity in each sequence shows a gradual fall as we pass from first to higher sequence members. The Condon curve that can be drawn through the strongest bands is of the type which is to be expected with such relative values of ω as occur here.

TABLE II
Vibrational Analysis of BiI bands

$v' \backslash v''$	0	1	2	3	4	$\Delta G(v')$
0	169.7 17230.1 193.4	17060.4 196.2 166.9				194.8
1	17423.5 187.8	17256.6 190.0	17088.4			188.9
2	17614.3 165.7	17446.6		17115.0		
3		188.6 17635.2 168.5	17466.7		17138.5	188.6
						$\Delta G(v'')$ 167.4 168.4



Bismuth iodide bands.

(*a*) New system.

(*b*) Morgan's system.

TABLE III

Intensity Distribution in the System

$\begin{smallmatrix} \diagup \\ v'' \\ \diagdown \end{smallmatrix}$	0	1	2	3	4
0	10	6			
1	8	4	5		
2	4	4		4	
3		3	1		2

MORGAN'S SYSTEM

As in the other system, the bands in this system appear clearly degraded towards the red while in all the sequences the sequence degradation is towards the violet. All the bands recorded by Morgan are obtained here together with 3 new bands, whose wavelength, intensity and other data are shown in the Table IV.

TABLE IV

Wavelength	Int.	Wavenumber	Classification
4160.4	2	24029.4	5,2
68.0	3	23985.6	3,0
4246.2	1	23543.9	5,5

ELECTRONIC STATES IN BISMUTH HALIDES

Investigations on the halides of the related elements N, P, As, etc. are few. A band system between λ 6550— λ 5456 attributed to the molecule NBr is known from the work of Elliott (1939). Band spectra of the halides of phosphorus and arsenic are not so far known. Of the halides of antimony, Howell and Rochester (1939) analysed a triplet system of SbF in the visible region between λ 5200— λ 3600, which was suggested as due to a transition between triplet electronic levels. They also analysed a similar triplet system in the ultraviolet between λ 2700— λ 2200. The final state is common in both the triplet systems and is suggested to be a probable $^3\pi$. They stated that the multiplet separations of the states are not known nor is the nature of other electronic levels. Two band systems between λ 5600— λ 4600 attributed to SbCl have been analysed by Ferguson and Hudes (1940). In any of the

above investigations, however, no definite information regarding the electronic states of the halides of these elements is available in order to identify by comparison the electronic states of bismuth halides. But an idea of the electronic states of the halides of bismuth can be obtained from a knowledge of the electronic states of the BiH molecule. Heiner (1935) established two systems in BiH with a common $^1\Sigma$ upper state as due to the transitions $^1\Sigma - ^1\Sigma$ and $^1\Sigma - ^1\Pi$, the lower $^1\Sigma$ being the ground state. Hence the ground state of the halides of bismuth may, in all probability be a $^1\Sigma$. A consideration of the ground state configurations of the halides of the elements Hg, Tl, Pb etc., lying in the same horizontal row of the periodic table would also lead to the same view. The ground state of the mercury halides can be written as $\sigma^2\Pi^4\sigma$, $^2\Sigma^+$. By the successive addition of one electron to the above configuration, the ground state configurations of the halides of the other elements are

$$\sigma^2\pi^4\sigma^2, \quad ^1\Sigma \quad (\text{thallium halides})$$

$$\sigma^2\pi^4\sigma^2\pi, \quad ^2\pi_{(r)} \quad (\text{lead } ,,)$$

$$\sigma^2\pi^4\sigma^2\pi^2, \quad ^1\Sigma, \quad ^1\Delta \quad \text{and} \quad ^3\Sigma^- \quad (\text{bismuth } ,,)$$

By analogy with the $^1\Sigma$ ground state established in the halides AlCl ; Holst, (1934) and AlBr (Jennergreen, 1948), Howell (1937) suggested that the ground state of the thallium halides is a $^1\Sigma$. Ferguson (1928) analysed two systems of SnCl with a common lower state with a separation of 2360 cm., while Rochester (1938) established a $^2\Pi$ ground state in the spectrum of PbF with a doublet separation of 8270 cm⁻¹. This indicates that $^2\Pi$ may probably be the ground state of lead halides. With the exception of BiF, each of the other halides of bismuth is known to give two systems of bands which have a common ground state. The simple, well marked rotational structure observed in the low frequency system of BiF indicates, as Howell remarked, that the transition involved may be between singlet levels. Hence the ground state of bismuth halides is most probably $\sigma^2\pi^2, ^1\Sigma$. Excitation of the π electrons of the normal configuration into the next higher orbits gives the electronic states

$$\sigma^2\pi^4\sigma^2\pi\sigma, \quad ^1\Pi^3\Pi_{(r)}$$

and

$$\sigma^2\pi^4\sigma^2\pi^0\sigma^2, \quad ^1\Sigma^+$$

The $^1\Pi$ and $^1\Sigma^+$ states are most probably the upper levels of the two observed band systems in bismuth halides.

$$\pi\sigma, \quad ^1\Pi \rightarrow \pi^2, \quad ^3\Sigma \quad (\text{low frequency system})$$

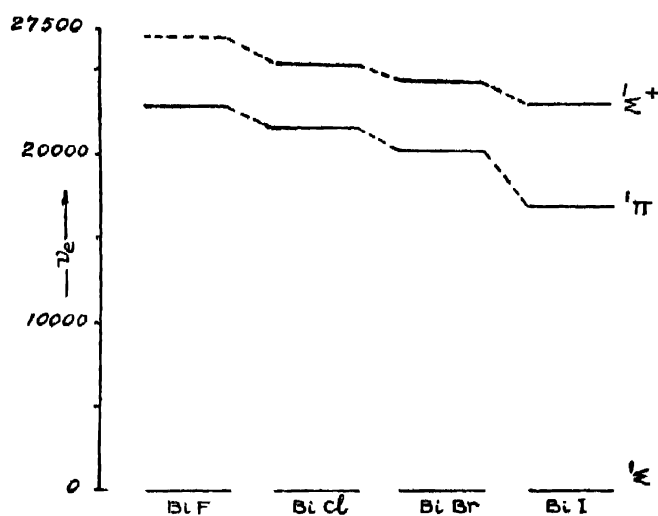
$$\sigma^2, \quad ^1\Sigma^+ \rightarrow \pi^2, \quad ^1\Sigma \quad (\text{high } ,,)$$

The first two excited states of BiH molecule also $^1\Pi$ and $^1\Sigma$ established from a study of the rotational structure of the bands, which probably gives further

justification for the proposed identification of the energy states in the case of bismuth halides. The transition ${}^3\Pi_{(r)} - {}^1\Sigma$ may be weak and lie in the near infra-red.

One might also regard the two systems in bismuth halides as due to the transitions ${}^3\Pi_0 - {}^1\Sigma$ and ${}^3\Pi_1 - {}^1\Sigma$, the other component ${}^3\Pi_2 - {}^1\Sigma$ lying probably in the infra-red. But the simple marked rotational structure observed by Howell in BiF bands indicates clearly that the transition may be between singlet levels. This supports the assignment of the two systems to the transitions ${}^1\Pi - {}^1\Sigma$ and ${}^1\Sigma - {}^1\Sigma$.

As the energies of dissociation cannot be extrapolated with accuracy in these halides, no attempt has, therefore, been made to correlate the above electronic states with those derivable from the most probable products of dissociation.



ELECTRONIC ENERGY LEVELS IN BISMUTH HALIDES.

FIG. 1

An energy level diagram for the halides of bismuth is given in Fig. 1. A glance at this diagram shows that the corresponding energy levels are lower, the heavier the molecule, which is to be expected.

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